Growth and decay of Modified starch Production line free radicals under microwave irradiation

ABSTRACT: The growth and decay of rice starch free radicals during storage under Microwave drying machinerywere studied. The relative number and structure of free radicals in microwave treated starch were analyzed by means of electron paramagnetic resonance (EPR) and spectrum fitting software. The results showed that Starch Treated by microwave could produce free radicals which existed for a long time at room temperature; Starch Treated by microwave could produce carbon-centered free radicals; the number of free radicals increased at 1 600 W (160 W/g) power more than 800 W (80 W/g) power; and the free radicals increased at the stopping of microwave treatment. Three free radicals were isolated from microwave-treated starch. The main component was the free radicals centered on the glucose ring C1.

As a new heating technology, microwave drying equipment has been widely used in all aspects of daily household and industrial applications. Because of its simple and rapid operation, microwave is widely used in food processing, such as food thawing, drying, baking, enzyme inactivation and sterilization. Starch drying equipment is one of the main ingredients of most processed foods. It was found that starch could produce free radicals in a certain intensity of energy field, and the size and time of energy acceptance could affect the production of free radicals. For example, high temperature heating, X rays, gamma rays and ultraviolet radiation can all cause starch free radicals. It is well known that microwave irradiation can also induce free radical reactions in starch. Free radical reactions may produce a kind of radicals with very short half-life and a kind of long half-life. Free radicals with short half-life can cause damage to biological cells and lead to disease. Free radicals with long half-life in macromolecule carbohydrates can be used as free radical traps to neutralize harmful high reactivity. Sexual radicals. Free radicals are related to starch chemical reactions, for example, starch thermal degradation leads to intramolecular or intermolecular dehydration caused by free radical reactions, will produce furan, small molecules of aldehydes and ketones, as well as C O2, C O, H2O gas. Therefore, it is of great significance to understand the effect of microwave treatment on free radicals produced by starch and the attenuation characteristics of free radicals during storage, and to control the quality and flavor of microwave food.

There have been many studies on microwave starch, such as properties of starch granules, rheological and swelling properties, thermodynamics and dielectric properties of starch. These evidences indicate that microwave irradiation will inevitably change the starch granule and even the molecular structure. However, there are few reports about the growth and attenuation of free radicals produced by rice starch in microwave field at home and abroad. In this study, the free radical formation of rice starch with low water activity and the attenuation of starch free radical during storage at room temperature were investigated under the civil microwave frequency (2 450 MHz). In this experiment, the types, components and relative quantities of free radicals were detected by EPR, and the molecular structure information of starch free radicals was obtained by software fitting analysis, so as to deduce the composition changes of starch free radicals during the growth and decay process.

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(1) The water content of rice starch was regulated to regulate the water activity of starch. The rice starch was put into an open beaker and sealed and balanced for 2 weeks on a ceramic partition with a K2SO4 saturated solution under it. The water activity of starch was determined by GBX FA-st lab water activity meter.

(2) The preparation of microwave-treated rice starch lays 2.0 g of rice starch in an open glass dish with an average thickness of 1.5 mm. Five Petri dishes were placed in the middle of the microwave chamber under microwave irradiation. At 2 450 MHz, the Petri dishes were treated with 1 600 W (160 W/g) and 800 W (80 W/g) power for 1-5 min, respectively. At the end of the microwave, the starch samples in five dishes were mixed evenly, and the free radical signal was determined immediately or stored for a certain time. The storage condition of the sample is room temperature (around 20 degrees Celsius).

(3) The free radicals were accurately weighed (60.0 (+ 0.5) mg by paramagnetic resonance in a nuclear magnetic resonance (NMR) sample tube with an inner diameter of 3 mm, and the sample tube was placed in a resonant cavity. The microwave frequency of the instrument is 9.85 GHz, and the debugging frequency is 100 kHz. The central magnetic field, sweep field width, modulation amplitude (MA), gain and microwave power were 351 mT, 10 mT, 0.6 T, 3.17 *105 and 20 mW respectively. The g value was determined by comparative method. The standard sample (Bruker's Mark, g = 1.9800) with known g value and the sample to be measured were placed in the resonator, and the spectrum was recorded. The g value of the sample was obtained by comparing with Mark. The g value of the sample to be tested can be obtained from the following formula. GX beta = GS Hs

On the other hand

Hs

Formula: subscript s and x represent standard samples and samples to be tested respectively, and beta is Bohr magneto. The signal intensity is the peak-height difference of the first derivative of the electron paramagnetic resonance (EPR) line. EPR signal simulation uses EasySpin 4.5.3 free radical processing software based on the Matlab R2013a (The MathWorks, Inc.) platform. The G error of the software is + 0.005, and the hyperfine constant A error is + 0.1 mT.

Two, results and analysis

(1) analysis of starch free radicals in microwave heating

348 350 352 354 / mT A 348 350 352 354 / mT B Sim Exp A. raw starch signal; B. signal 5 min after 1 600 W processing. The EPR spectra of rice starch (Exp), signal fitting spectra () and signal fitting spectra (Sim) showed no obvious signal peaks. The free radical signal produced by microwave treatment is shown in Fig. 1B. Comparing the spectrum of starch free radicals obtained in this experiment with that of abanowska and other thermal free radicals, the peak shape of the spectrum is similar. The signal G value of the sample free radicals calculated by the comparison method and the standard sample Mark g value in the paramagnetic resonance

spectrometer is the typical g value of starch carbon free radicals, so it can be used to determine the sample. The free radicals produced by microwave treatment of starch are carbon-centered radicals, which are also consistent with the experimental results of microwave treatment of potato starch and corn starch by Dyrek et al. 348 352 354 / mT 116 2014, Vol. 35, No. 13 Food Science Basic Research 348 352 / mT / mT / rice starch free radical signal main component, obviously from the microwave treatment of rice starch EPR can be seen that the starch free radical is not a single component. Instead, it is a combination of multiple components. Through signal simulation, 3 main components are analyzed. It can be seen that signal I is the free radical formed after the removal of alpha hydrogen from the position of glucose ring C1. The beta hydrogen atom on C2 splits the free electrons on C1 to form a double peak. However, as the split constant is small, the apparent signal I still presents a heavy peak pattern. Signal II shows a hyperfine structure (HFS) line with four peaks, which is composed of C6 free radicals in the glucose side chain. C6 removes one alpha hydrogen to form free radicals, and the free electrons on C6 are produced by another alpha hydrogen and beta hydrogen on C5, respectively, resulting in the formation of HFS structure. Signal III is formed by intramolecular dehydration of H atoms at C2 and OH groups at C3, resulting in a double bond that allows the electrons in Component I to be delocalized onto the PI bond. Therefore, the increase of component III is generally accompanied by a decrease in component I.

(2) the effect of microwave heating time on the growth of starch free radicals.

The effect of microwave heating time on the growth of starch free radicals was studied. The paramagnetic resonance signals of rice starch samples with water activity of 0.7 were processed at microwave power of 1 600 W and 800 W for 1-5 min, respectively. The trend of time evolution. It can be concluded that when starch was irradiated by microwave for 1 to 2 minutes, the signal almost did not increase, indicating that there was no stable free radical production in starch. This may be because the system has not yet converted electromagnetic energy into enough thermal and chemical energy to stimulate free radical reactions, or because the water in the system will produce free radical quenching. In the initial stage of radiation, considering the existence of water, the sample has a large dielectric constant, which can effectively convert the energy of electromagnetic field into heat, so the sample temperature rises rapidly. After microwave treatment for 3 min, only signal I and signal II, 87% and 13% respectively, were found in the free radical signal. It was proved that the main component of the free radical was dehydrogenation products of C1 position of glucose ring in starch molecule, and the other part was the free radical produced by dehydrogenation of C6 position of side chain. In the second to fourth minute of microwave radiation, the free radicals increase rapidly, which may be the chain effect caused by multiple factors. As the temperature increases, the activity of molecules increases and is more easily stimulated by heat and energy from other sources. The third component appeared in the signal at 4 min after the starch molecule absorbed energy, which was due to the dehydration of hydrogen on the glucose ring C2 and hydroxyl groups on the C 3 to form a C = C bond. Thus the unpaired electrons on the C1 were no longer subjected to the splitting of H atoms on the C2, and the reduction of oxygen atoms and the formation of double bonds in the molecule made them self-contained. The g value of the base is reduced relative to component I. At the 5th minute after microwave irradiation, the water activity decreased to 0.05, and the ratio of signal III increased significantly from 2% to 4%, while the ratio of C6 radical decreased to about 9%, indicating that the dehydrogenation rate of

C1 was slightly higher than that of C6, and part of signal I was converted to signal III, suggesting that C2-C3 was between. Generation of double bonds. At the same time, a large number of free radicals already exist in starch matrix, which enhances the dipole-dipole interaction between free radical electrons, leading to part of the signal broadening, which may result in the apparent growth of free radicals slowing down at 4-5 minutes. Table 1 Fitting results of EPR free radical signal parameters of starch microwave treatment after microwave treatment For rice starch processed at 800 W, almost 2 min at the initial stage.

The growth of free radicals is not detected. After 2 minutes, the growth trend of free radicals was similar to that of 1 600 W, but the growth rate was obviously slower than that of free radicals at 1 600 W. After 4 minutes, the difference between the amount of starch free radicals treated at 800 W and that treated at 1 600 W tended to be constant. Table 1 shows that the fitting results of 800 W power treatment radicals are almost different, and the contents of their components are the same, 92% of C1 radicals and 8% of C6 radicals, respectively. 2.3 Effect of storage time on the decay of starch free radicals after microwave treatment_Basic research on the decay characteristics of starch free radicals during storage_Food Science 2014, Vol. 35, No. 13117. Starch samples treated with microwave for 5 min at 1 600 W and 800 W were stored at room temperature in dark for 0-120 days, respectively. Paramagnetic resonance detection. With the prolongation of storage time, the dipole-dipole interaction between a large number of free radicals in starch matrix weakens gradually, which makes the original undetected signal of free radicals appear. The amount of Starch Treated with 800 W was significantly higher than that of Starch Treated with 800 W, so the effect of delayed growth of free radicals was more significant in Starch Treated with 1 600 W. After the first to fifth days, the free radical growth trend disappeared and began to decay slowly. The number of free radicals treated at 1 600 W decreased to the number at the end of microwave treatment in three weeks, while the number of free radicals treated at 800 W decreased to the number at the end of microwave treatment in about 9 days. At the 16th week, the free radical content of 1 600 W treated samples was still higher than that of 800 W treated samples. Further analysis of free radicals composition during decay showed that component III of 1 600 W treated rice starch gradually decreased to disappear within 5 days during storage. This is the opposite of the formation process of component III during microwave treatment. It is speculated that this phenomenon is due to the fact that during storage, the C2 = C3 bond formed by dehydration of glucose molecules gradually absorbs water in the environment, the double bond is reduced, and the component III is gradually converted to the free radical form of component I. The results showed that the free radical components containing double bonds were unstable during storage, while the C1 radical and C6 radical of glucose ring were relatively stable. After 800W treatment, the composition of rice starch did not change greatly either in the free radical growth stage or in the decay stage. The main component of rice starch was component I, which accounted for more than 90% of the total free radicals and contained some free radical components of side chains.

Three. Conclusion

In this study, the free radicals of Rice Starch Treated by microwave were detected, and it was verified that microwave treatment could produce stable free radicals at room temperature for a long time. It is determined that free radicals of rice starch are carbon free radicals. The structure of 3 components of rice starch free radicals. It is found that the number of free radicals increases with time and the difference is stable under different microwave power. It was found that the decrease of dipole action of free radicals in starch matrix would lead to the increase of signal in the early storage period, the decrease of signal in the middle and late storage period, and the change of free radical composition. Free radicals discussed in this experiment are stable free radicals with relatively long half-life, but not short half-life free radicals. Because of its lively nature, it is quenched and quenched in a few seconds, so it is difficult to detect. In the future, our research group can explore appropriate trapping methods to prolong the half-life of active radicals and then detect their quantity and composition, which is of great significance to improve the research of the growth and decay of free radicals produced by microwave treatment of starch.